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SYNTHESIS AND MOLECULAR STRUCTURE OF HYDRIDO(TETRAHYDROBORATO)(1,1,1-TRIS(DIPHENYLPHOSPHINOMETHYL)ETHANE)-IRON(II)

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Summary

Sodium tetrahydroborate reacts with iron(II) tetrafluoroborate and 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) to give the complex (triphos)-$FeH(BH_4)$ whose molecular structure, determined from X-ray data consists of monomolecular units in which the iron atom is six-coordinated by the three phosphorus atoms of the ligand, two hydrogen atoms of the BH_4 group, and a hydridic hydrogen atom. Variable temperature ^{31}P NMR spectra reveal stereochemical non-rigidity of the complex in solution.

It has previously been shown that sodium tetrahydroborate reacts with iron(II) halides and the tripod-like triphosphine 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) to form the dinuclear complex [(triphos)Fe(μ-H)$_3$Fe(triphos)]BPh_4 [1].

Now we describe the hydrido tetrahydroborato complex (triphos)FeH(BH_4), obtained by reaction of sodium tetrahydroborate with iron(II) tetrafluoroborate and triphos. Some transition metal complexes containing both tetrahydroborate and hydride ligands are known in which monotertiary phosphines are present [2].

A solution of triphos and $Fe(H_2O)_6(BF_4)_2$ (molar ratio 1/1) in tetrahydrofuran/ethanol was treated with an excess of $NaBH_4$ (Fe/$NaBH_4$ ca. 1/10) at 60°C. Distillation of the solvent gave red crystals of (triphos)FeH(BH_4). The complex, which is air sensitive, is fairly soluble in organic solvents such as benzene and tetrahydrofuran, and slowly decomposes in the solution.

The molecular structure of the compound has been determined by X-ray diffraction. The crystals (which are isomorphous with a series of complexes in

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which the triphos is present, such as (triphos)NiI [3], (triphos)Co(BH_4) [4] and (triphos)Cu(BH_4) [5]) are orthorhombic, space group $Pn2_1a$, with a = 20.803(7), b = 16.964(5), c = 10.242(3) Å and Z = 4. Data collection was carried out on a Philips computer controlled PW 1100 diffractometer using the $\omega-2\theta$ scan technique and graphite monochromated Mo-K_α radiation. An absorption correction (μ(Mo-K_α) 5.4 cm^{-1}) giving transmission factors ranging from 0.95 to 0.87 was applied. The structure was solved by the heavy atom technique and refined by full-matrix least-squares refinements. The tetrahydroborate and hydridic hydrogen atoms, located from a difference Fourier map (sen $\theta/\lambda < 0.35$ Å^{-1}) were successfully refined. Refinements converged at the R and R_w factors values of 0.042 and 0.041 for the 1191 reflections ($2\theta \leqslant 40°$) having $I \geqslant 3\sigma(I)$.

The molecular structure consists of monomolecular units of (triphos)FeH(BH_4). A perspective view of the molecule is shown in Fig. 1. The iron atom is coordinated by the three phosphorus atoms of the triphos ligand, two hydrogen atoms of the tetrahydroborate group and a hydridic hydrogen atom, in a distorted octahedral environment. The bidentate attachment of the BH_4 ion is unambiguously confirmed by the Fe—B distance, for which the value of 2.16(2) Å, is comparable with those of 2.21(3) and 2.44(2) Å reported for (triphos)Co(BH_4) [4] and (triphos)Cu(BH_4) [5]. These compounds are isomorphous with the title complex, and contain a bidentate and a monodentate BH_4 group, respectively.

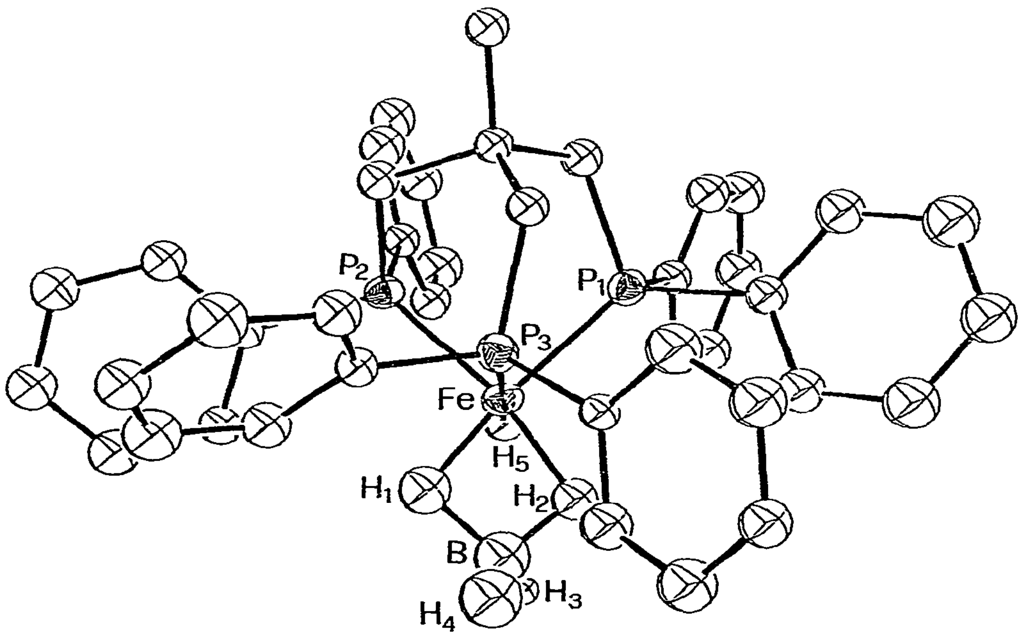

Fig. 1. Perspective view of the complex molecule (triphos)FeH(BH_4). ORTEP drawing with 30% probability ellipsoids. Important bond distances (Å) and angles (deg): Fe—P(1) 2.175(3), Fe—P(2) 2.162(4), Fe—P(3) 2.230(4), Fe—H(1) 1.58(11), Fe—H(2) 1.65(11), Fe—H(5) 1.41(10), Fe—B 2.16(2), P(1)—Fe—P(2) 88.2(2), P(1)—Fe—P(3) 90.3(1), P(2)—Fe—P(3) 92.9(1), P(1)—Fe—H(1) 170(4), P(2)—Fe—H(2) 154(4), P(3)—Fe—H(5) 178(4), H(1)—Fe—H(2) 71(5).

The solid state IR spectrum of the complex in the M—H stretching vibrations region shows a strong doublet at 2320 and 2380 cm^{-1} and a strong band at 1910 cm^{-1}, attributable to B—H$_t$ and B—H$_b$ stretching absorptions, respectively, in agreement with a bidentate structure having approximately C_{2v} local symmetry [6].

Variable temperature ^{31}P NMR spectra in tetrahydrofuran solution indicate dynamic behaviour for the (triphos)FeH(BH_4) molecule. The ^{31}P{^{1}H} low temperature spectrum (–80°C) [7] consists essentially of an A_2X pattern with a doublet at δ 79 ppm and a triplet at δ 35.5 ppm (intensity ratio 2/1; J(P—P) 27.8 Hz; δ for the free ligand –30.2 ppm). As the temperature increases these resonances broaden and decrease while a broad band centered at ca. δ 62 ppm (–10°C) appears. At +50°C the spectrum only consists of a broad singlet at δ 64 ppm (δ for the free ligand –26.3 ppm) indicating the magnetical equivalence of the three phosphorus atoms.

^{1}H NMR studies are in progress to throw light on the nature of this dynamic system.

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